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(54) POSITIVE ACTIVE MATERIAL FOR LITHIUM SECONDARY BATTERY AND LITHIUM SECONDARY BATTERY

(57)Abstract:
PURPOSE: To provide a positive active material capable of decreasing self discharging and increasing cycle performance of a lithium secondary battery.
CONSTITUTION: A lithium-containing composite oxide having layer crystal structure and represented by LixNiaCobMcO2 (0.8≤x≤1.2, 0.01≤a≤0.99, 0.01≤b≤0.99, 0.01≤c≤0.3, 0.8≤a+b+c≤1.2, and M is at least one element selected from the group comprising Al, V, Mn, Fe, Cu, and Zn.) is used as a positive active material for a lithium secondary battery.

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CLAIMS

[Claim(s)]
[Claim 1] Positive active material for lithium secondary batteries characterized by consisting of a lithium content multiple oxide which has crystalline-lamellas structure and is expressed with the degree type LixNiaCobMcO 2 (at least one sort of elements with which 0.8<=x<=1.2 , 0.01<=a<=0.99 , 0.01<=b<=0.99, 0.01<=c<=0.3 , 0.8<=a+b+c<=1.2 , and M are chosen from aluminum, V, Mn, Fe, Cu, and Zn).
[Claim 2] Positive active material for lithium secondary batteries according to claim 1 whose crystalline-lamellas structure is an alpha-NaFeO 2 mold crystal structure.
[Claim 3] The lithium secondary battery which used the lithium or the lithium compound as a negative-electrode active material, and used positive active material according to claim 1 or 2 as positive active material.

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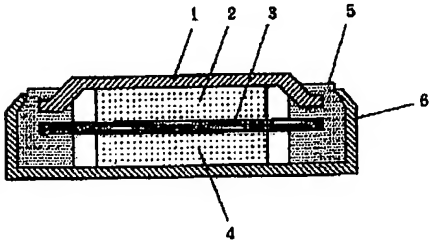
R3m

Drawing selection drawing 1



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CLAIMS

[Claim(s)]
[Claim 1] Positive active material for lithium secondary batteries characterized by consisting of a lithium content multiple oxide which has crystalline-lamellas structure and is expressed with the degree type LixNiaCobMcO 2 (at least one sort of elements with which 0.8<=x<=1.2 , 0.01<=a<=0.99 , 0.01<=b<=0.99, 0.01<=c<=0.3 , 0.8<=a+b+c<=1.2 , and M are chosen from aluminum, V, Mn, Fe, Cu, and Zn).
[Claim 2] Positive active material for lithium secondary batteries according to claim 1 whose crystalline-lamellas structure is an alpha-NaFeO 2 mold crystal structure.
[Claim 3] The lithium secondary battery which used the lithium or the lithium compound as a negative-electrode active material, and used positive active material according to claim 1 or 2 as positive active material.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to a lithium content multiple oxide useful as positive active material of a lithium secondary battery.
[0002]
[Description of the Prior Art] The lithium secondary battery attracts attention in various electronic equipment as a portable power source which can attain high power and a high energy consistency and in which charge and discharge are possible, and research is advanced actively.
[0003] A lithium or a lithium compound is used for a lithium secondary battery as a negative-electrode active material, and, generally a dope, the conductive polymer which can be dedoped or stratified compounds (a carbon material, metallic oxide, etc.), the metal lithium, or the lithium alloy is reversibly used in the lithium (a lithium ion is included) as the negative-electrode ingredient.
[0004] as the positive active material which forms a positive electrode on the other hand -- a spinel -- a relative -- the multiple oxide of a dope, and the transition metals and the lithium which can be dedoped is used in lithiums, such as LixMeO2 (Me=Co, nickel) (JP,63-59507,B) which has LiMn 2O4 which has the crystal structure, and a layer system.
[0005] In such a lithium secondary battery, since it is dependent on an electrode active material or the electrolytic solution, preservation properties, such as a self-discharge property and structural stability, and the cycle property of a cell have indispensable amelioration of an electrode active material or the electrolytic solution for an improvement of these properties. Then, various proposals are made about these from before.
[0006] For example, since the potential more than 4.0Vvs(es).Li/Li+ being shown and the amount of insertion desorption of a lithium are large when a lithium is desorbed, LixMeO2 (Me=Co, nickel) which has an above-mentioned layer system about positive active material serves as an oxide useful as positive active material for nonaqueous electrolyte lithium secondary batteries, but since electrode potential is high and decomposition and side reaction of the electrolytic solution are easy to be triggered, it has the trouble on self-discharge or safety. Then, the attempt which permutes some Co elements in LixCoO2 until now with dissimilar metals, such as aluminum, In, Sn, W, Mn, Ta, Ti, and Nb, is made. more -- concrete -- JP,63-121258,A -- AxByCzDwO2 (A -- alkali metal -- 0.05<=x<=1.10 [ ] --) B -- transition metals -- 0.85<=y<=1.00 C -- aluminum, In, or Sn -- 0.001<=z<=0.10 D -- alkali-metal [other than A]; -- transition-metals [other than B]; -- IIa group element; or aluminum -- IIIb-VIb except In, Sn, C, N, and O 0.001<=w<=0.10 is proposed by the element of a group's 2-6th periods. To JP,3-201368,A LixCo1-yMyO2 (0.85<=x<=1.3 , 0.05<=y<=0.35 , and M are chosen from W, Mn, Ta, Ti, and Nb at least a kind) is proposed.
[0007] moreover, it inquires also about replacing the cobalt in the multiple oxide containing a lithium and cobalt with cheaper nickel -- having -- **** -- for example, LixNiyCo1- yO2 (0<=y<=1) (J. Power.Sources and 43-44,595 (1993)), LixNiO2 (J. 140 Electrochem.Soc. and 1862 (1993)), etc. are proposed. Moreover, LixMnyNi1-yO2 (0<=y<=0.5) (Solid State Ionics and 57,311 (1992)) which

permuted nickel by manganese is proposed.
[0008]
[Problem(s) to be Solved by the Invention] However, depending on amelioration of the positive active material by the conventional dissimilar metal dissolution that a dissimilar metal permutes some nickel in the multiple oxide containing a lithium and nickel, the property of positive active material cannot fully be raised, and lowering of discharge capacity and the pulverization of an active material pose a problem. They have come [therefore,] to be put in practical use.
[0009] This invention tends to solve the technical problem of such a conventional technique, and aims at offering the positive active material which can raise preservation properties, such as the self-discharge property of a lithium secondary battery, and structural stability, and the cycle property of a cell.
[0010]
[Means for Solving the Problem] this invention person came to complete a header and this invention for the ability of the above-mentioned object to be attained by permuting the nickel in the multiple oxide of LixNiyCo1-yO2, and some cobalt [at least] by the specific element.
[0011] That is, this invention has crystalline-lamellas structure and offers the positive active material for lithium secondary batteries characterized by consisting of a lithium content multiple oxide expressed with the degree type LixNiaCobMcO 2 (at least one sort of elements with which $0.8<=x<=1.2$, $0.01<=a<=0.99$, $0.01<=b<=0.99$, $0.01<=c<=0.3$, $0.8<=a+b+c<=1.2$, and M are chosen from aluminum, V, Mn, Fe, Cu, and Zn).
[0012] Moreover, the lithium secondary battery which used such positive active material for the positive electrode, and used the lithium or the lithium compound as a negative-electrode active material is offered.
[0013] Hereafter, this invention is explained to a detail.
[0014] The positive active material of this invention permutes the nickel in the multiple oxide of LixNiyCo1-yO2, and some cobalt by at least one sort of elements chosen from aluminum, V, Mn, Fe, Cu, and Zn, and is expressed with LixNiaCobMcO2. Here, x takes the numeric value of the range of 0.8-1.2, and is 1 preferably. Since it is desirable from the point of reducing a manufacturing cost since the rate of cheap nickel can be made [many], but a self-discharge property and a cycle property will fall if the rate of nickel increases too much so that it enlarges to b and c, a makes a 0.01 to 0.99 range, and 0.01 to 0.99 and c are set to 0.01 to 0.3, and it sets a+b+c to 0.8-1.2 for b. Since effectiveness of this invention cannot be acquired if this c is too small, but the layer-like crystal structure will collapse if too large, and cell capacity falls, it is not desirable.
[0015] Moreover, this lithium content multiple oxide shall have the layer-like crystal structure. Preferably, it shall have the alpha-NaFeO 2 mold crystal structure of LixCoO2 and resemblance. Thereby, a lithium can be reversibly used as a dope and the positive active material which can be dedoped.
[0016] Although there is especially no limit about the manufacture approach of such a lithium content multiple oxide, for example, the metal salt of a raw material can be mixed so that the mole ratio of each metal may serve as a predetermined value, and it can obtain by calcinating the mixture.
[0017] The lithium content multiple oxide of this invention can be used as positive active material like the conventional Li content multiple oxide. For example, it mixes with a well-known electric conduction agent and a well-known binder, and will become useful as a positive electrode of a lithium secondary battery by fabricating. In this case, the lithium content multiple oxide of this invention can be used also as positive active material of the lithium cell of which types, such as a nonaqueous electrolyte lithium secondary battery and all solid-state lithium secondary batteries.
[0018] The lithium content multiple oxide of above-mentioned this invention can be used for the lithium secondary battery of this invention as positive active material, and the other configuration can be made to be the same as that of the conventional lithium secondary battery.
[0019] That is, a lithium or a lithium compound is used as a negative-electrode active material. Therefore, a negative electrode constitutes a lithium using a dope, the ingredient which can be dedoped, a metal lithium, or a lithium alloy. A lithium can be used for polymers, such as carbonaceous

ingredients, such as pyrolytic carbon, corks (pitch coke, needle coke, petroleum coke, etc.), graphite, glassy carbon, an organic high-molecular-compound baking object (what calcinated and carbonized phenol resin, furan resin, etc. at suitable temperature), a carbon fiber, and activated carbon, or polyacethylene, and polypyrrole, etc. among the components of such a negative electrode as a dope and an ingredient which can be dedoped, for example. Moreover, a lithium-aluminium alloy, a lithium-indium alloy, etc. can be used as a lithium alloy. Moreover, it faces forming a negative electrode from such an ingredient, and a well-known binder etc. can be added.

[0020] Moreover, when using nonaqueous electrolyte for a lithium secondary battery, the thing same as the nonaqueous electrolyte as the nonaqueous electrolyte currently used for the conventional nonaqueous lithium secondary battery can be used. That is, as a non-aqueous solvent of nonaqueous electrolyte, propylene carbonate, ethylene carbonate, butylene carbonate, vinylene carbonate, gamma-butyrolactone, a sulfolane, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, 2-methyl tetrahydrofuran, the 3-methyl -1, 3-dioxolane, methyl propionate, methyl butyrate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, etc. can be used, for example. It is desirable to use chain-like carbonate, such as annular carbonate, such as propylene carbonate, ethylene carbonate, butylene carbonate, and vinylene carbonate, or dimethyl carbonate, diethyl carbonate, and dipropyl carbonate, for an electrical potential difference from a stable point especially. Moreover, such a non-aqueous solvent can be used combining one sort or two sorts or more.

[0021] Moreover, it is desirable especially to be able to use LiClO4, LiAsF6, LiPF6, LiBF4, LiCF3SO3, and LiN(CF3SO2)2 grade, among these to use LiPF6 and LiBF4 as an electrolyte dissolved in a non-aqueous solvent, for example.

[0022] The cell of this invention is not limited especially about a cell configuration. It can be made various configurations, such as cylindrical, a square shape, a coin mold, and a carbon button mold.

[0023]

[Function] The positive active material of this invention is expressed with LixNiaCobMcO2 (at least one sort of elements with which $0.8<=x<=1.2$, $0.01<=a<=0.99$, $0.01<=b<=0.99$, $0.8<=c<=0.3$, $0.08<=a+b+c<=1.2$, and M are chosen from aluminum, V, Mn, Fe, Cu, and Zn). Since this lithium content multiple oxide consists of what was permuted by specific element called aluminum, V, Mn, Fe, Cu, or Zn, it can obtain cheaply the nickel in the multiple oxide of LixNiyCo1-yO2, and some cobalt [at least] as compared with LixCoO2. Moreover, self-discharge is notably controlled by stabilization of the crystal structure by dissimilar metal dissolution, and it becomes that whose cycle property improved.

[0024]

[Example] Hereafter, an example explains this invention concretely.

[0025] In order to compound example 1 positive active material, after having carried out weighing capacity so that the mole ratio of Li:nickel:Co:aluminum might be set to 10:8:1:1, and fully mixing, it put in into alumina crucible, and in the oxygen ambient atmosphere, by 750 degrees C, the lithium nitrate, the nickel carbonate, the commercial tricobalt tetroxide, and the commercial aluminum hydroxide of reagent chemicals were calcinated for about 15 hours, and carried out air cooling to the room temperature. When the obtained baking object was investigated by X-ray diffraction analysis, it has crystalline-lamellas structure and has checked that it was expected positive active material.

[0026] Thus, the obtained positive active material was used and the lithium secondary battery was produced as follows.

[0027] The compound positive active material was ground, and weighing capacity of the grinding object, graphite, and poly vinylidene fluoride was carried out at a rate of 90:7:3 by the weight ratio, and it mixed. Application-of-pressure molding was carried out circularly, the pellet was obtained, and the positive electrode was produced for these mixed fine particles with a diameter of 15mm by drying this at 120 degrees C under reduced pressure for 12 hours.

[0028] On the other hand, as a negative electrode, the thing with a diameter of 15mm pierced circularly was produced for the lithium foil with a thickness of 1.85mm. In nonaqueous electrolyte, what dissolved LiPF6 in propylene carbonate (PC) at a rate of one mol/l. was prepared. moreover -- as a separator -- the fine hole made from polypropylene -- the thin film was prepared.

[0029] And using these positive electrodes, a negative electrode, the electrolytic solution, and a separator, as shown in drawing 1 , on the other hand, the negative electrode 2 made from lithium metal was stuck to the negative-electrode can 1 by pressure, the positive electrode 4 was stuck to the positive-electrode can 6 by pressure, the separator 3 was allotted among two poles and the coin mold cell (2.5mm in the diameter of 20mm, thickness) was produced by stopping both cell cans through a gasket 5.
[0030] In order to compound example 2 positive active material, except having carried out weighing capacity of the lithium hydroxide, the nickel oxide, the commercial tricobalt tetroxide, and the commercial vanadium sesquioxide of reagent chemicals as a synthetic ingredient, so that the mole ratio of Li:nickel:Co:V might be set to 10:8:1.9:0.1, positive active material was compounded like the example 1, and the lithium secondary battery was produced further.
[0031] In order to compound example 3 positive active material, except having carried out weighing capacity of the lithium hydroxide, the nickel oxide, the commercial tricobalt tetroxide, and commercial manganese oxide of reagent chemicals as a synthetic ingredient, so that the mole ratio of Li:nickel:Co:Mn might be set to 10:7:2:1, positive active material was compounded like the example 1, and the lithium secondary battery was produced further.
[0032] In order to compound example 4 positive active material, except having carried out weighing capacity of the lithium hydroxide, the nickel carbonate, the commercial tricobalt tetroxide, and the commercial iron sesquioxide of reagent chemicals as a synthetic ingredient, so that the mole ratio of Li:nickel:Co:Fe might be set to 10:7:1:2, positive active material was compounded like the example 1, and the lithium secondary battery was produced further.
[0033] In order to compound example 5 positive active material, except having carried out weighing capacity of the lithium hydroxide, the nickel carbonate, the commercial tricobalt tetroxide, and commercial copper oxide of reagent chemicals as a synthetic ingredient, so that the mole ratio of Li:nickel:Co:Cu might be set to 10:7:2.5:0.5, positive active material was compounded like the example 1, and the lithium secondary battery was produced further.
[0034] In order to compound example 6 positive active material, except having carried out weighing capacity of the lithium nitrate, the nickel oxide, the commercial tricobalt tetroxide, and the commercial zinc oxide of reagent chemicals as a synthetic ingredient, so that the mole ratio of Li:nickel:Co:Zn might be set to 10:8:1.5:0.5, positive active material was compounded like the example 1, and the lithium secondary battery was produced further.
[0035] In order to compound example of comparison 1 positive active material, except having carried out weighing capacity of the lithium hydroxide, the commercial nickel oxide, and commercial tricobalt tetroxide of reagent chemicals as a synthetic ingredient, so that the mole ratio of Li:nickel:Co might be set to 10:9:1, positive active material was compounded like the example 1, and the lithium secondary battery was produced further.
[0036] In order to evaluate the cycle property of the cell obtained in the assessment examples 1-6 and the example 1 of a comparison, the charge-and-discharge cycle trial was performed on 1mA of charging currents, charge electrical-potential-difference 4.2V, 1mA of discharge currents, and the conditions of discharge-final-voltage 2.5V, and it asked for the capacity retention (%) for every predetermined charge-and-discharge cycle. This result is shown in drawing 2 .
[0037] Moreover, in order to evaluate the self-discharge property of each cell, it asked for the percentage reduction of the discharge capacity when saving at a room temperature for one week in the state of 4.2V charge as a rate of self-discharge. This result is shown in a table 1.
[0038]
[A table 1]

	自己放電率（%）
実施例1	5．8
実施例2	6．5
実施例3	6．9
実施例4	5．7
実施例5	6．0
実施例6	7．2
比較例1	8．7

Drawing 2 shows that the cell of an example receives the cell of the example 1 of a comparison, and the gap of a cycle property is also improving.

[0039] Moreover, each cell of an example was, while the average operating potential at the time of discharge was 3.5-4.0V, and it was the same as the cell of the example of a comparison. Therefore, like an example, also when a specific element permutes a lithium, nickel and the nickel of a cobalt content multiple oxide, or cobalt, it turns out that the same operating voltage as the case where it does not permute is obtained.

[0040] Furthermore, a table 1 shows that the self-discharge property of the cell of an example is also improving.

[0041]

[Effect of the Invention] If the positive active material of this invention is used as positive active material of a lithium secondary battery, it will become possible to raise preservation properties and cycle properties, such as the self-discharge property of a cell, and structural stability.

[Translation done.]